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Key Points:

- Hydroxylamine concentrations are significantly correlated with nitrous oxide concentrations in oxygenated waters
- In waters that likely were influenced by denitrification the correlation between hydroxylamine and nitrous oxide breaks down
- Hydroxylamine may be useful as an indicator for active in situ production of nitrous oxide by nitrification in the open ocean

Supporting Information:

- Figure S1

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Hydroxylamine as a Potential Indicator of Nitrification in the Open Ocean

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Abstract Hydroxylamine (NH₂OH), a short-lived intermediate in the nitrogen cycle, is a potential precursor of nitrous oxide (N₂O) in the ocean. However, measurements of NH₂OH in the ocean are sparse. Here we present a data set of depth profiles of NH₂OH from the equatorial Atlantic Ocean and the eastern tropical South Pacific and compare it to N₂O, nitrate, and nitrite profiles under varying oxygen conditions. The presence of NH₂OH in surface waters points toward surface nitrification in the upper 100 m. Overall, we found a ratio of 1:3 between NH₂OH and N₂O in open ocean areas when oxygen concentrations were >50 μmol/L. In the equatorial Atlantic Ocean and the open ocean eastern tropical South Pacific, where nitrification is the dominant N₂O production pathway, stepwise multiple regressions demonstrated that N₂O, NH₂OH, and nitrate concentrations were highly correlated, suggesting that NH₂OH is a potential indicator for nitrification.

Plain Language Summary Hydroxylamine (NH₂OH) is a short-lived intermediate in the nitrogen cycle. It could be a precursor of nitrous oxide (N₂O) in the ocean. Nitrous oxide (N₂O) is an important greenhouse gas and leads to the production of other nitrogen species that can deplete the ozone layer. In the ocean, N₂O can be produced by two processes—nitrification and denitrification, while only during nitrification, the oxidation of ammonia to nitrate, is NH₂OH involved. The key aim of this study is to decipher the role of NH₂OH as a potential indicator for N₂O production. We found out that NH₂OH is strongly correlated with N₂O in open ocean areas, where nitrification is the main N₂O pathway and can therefore be used as an indicator for active nitrification and in situ N₂O production.

1. Introduction

Hydroxylamine (NH₂OH) is a short-lived intermediate in the nitrogen cycle (e.g., Ward, 2008). During nitrification, the oxidation of ammonia (NH₃) to nitrate (NO₃[−]) in presence of oxygen (O₂), NH₂OH can be produced and consumed by ammonia-oxidizing bacteria (AOB): NH₃ → NH₂OH → NO → NO₂[−] → NO₃[−] (for review see Kuypers et al., 2018). Additionally, ammonia-oxidizing archaea (AOA) have been discovered to be widespread in marine environments, often outnumbering their bacterial counterparts by orders of magnitude (Wuchter et al., 2006). Vajjala et al. (2013) could show through combined physiological and stable isotope tracer analyses that NH₂OH is both produced and consumed during the oxidation of NH₃ to nitrite (NO₂[−]) by AOA, indicating that NH₂OH may be an intermediate in archaeal nitrification, too. However, the microbial pathway of archaeal nitrification and the role of NH₂OH in this process is largely unknown so far. Genes encoding the NH₂OH oxidoreductase complex similar to AOB have not been identified in AOA (Kozłowski et al., 2016; Stieglmeier et al., 2014). However, due to the short lifetime of NH₂OH of only a few hours in seawater (Butler et al., 1987, 1988), its presence in the water column is strongly indicative of in situ production, and therefore, NH₂OH might be interpreted as an indicator for active nitrification.

NH₂OH is also a potential precursor for nitrous oxide (N₂O), which is a strong greenhouse gas and a major contributor to ozone depletion in the stratosphere (Crutzen, 1970; IPCC WG2, 2013; Ravishankara et al., 2009). In the ocean N₂O can be produced by nitrification and denitrification: Under anoxic and suboxic conditions NO₃[−] is stepwise reduced by denitrifying bacteria to molecular nitrogen (N₂) via the reaction chain NO₃[−] → NO₂[−] → NO → N₂O → N₂. Under oxic to suboxic conditions, N₂O is produced during bacterial and archaeal oxidation of NH₃ to NO₂[−], the first step of nitrification (Löscher et al., 2012; Santoro et al., 2011). The prevailing view of bacterial ammonia oxidation is via a two-step enzymatic

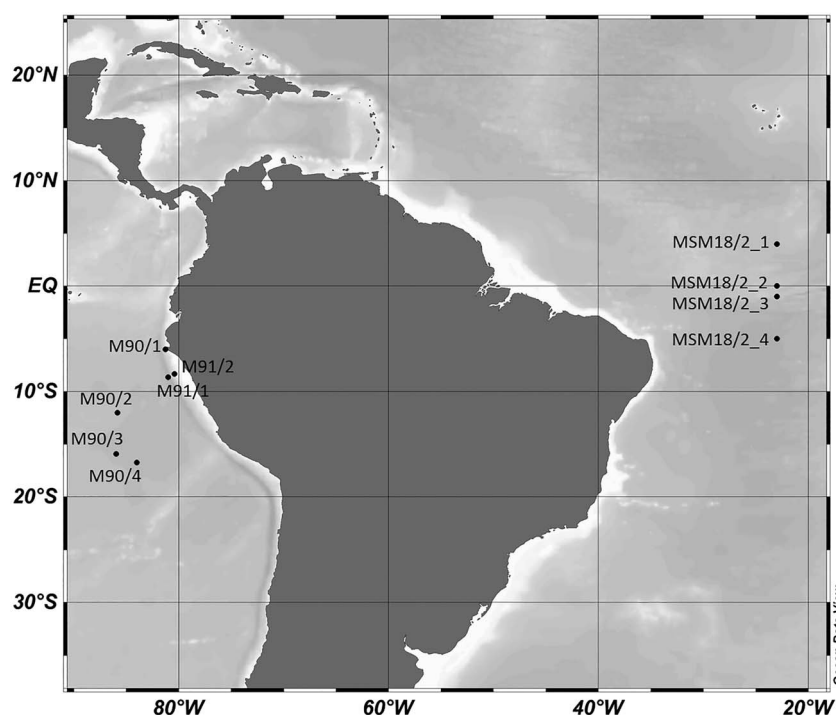


Figure 1. Map showing stations sampled (black dots) during the MSM 18/2, M90, and M91 cruises.

process involving the enzyme ammonia monooxygenase and hydroxylamine oxidoreductase (HAO; Arp & Stein, 2003). Here nitric oxide (NO) is arising from the incomplete oxidation of NH_2OH by HAO, in which NO is a HAO by-product that is further reduced to N_2O by the enzyme NO reductase (Stein, 2011). Recently, Caranto and Lancaster (2017) suggested that NO is an intermediate of NH_3 oxidation to NO_2^- and not a by-product. Their results showed that under aerobic conditions most of the NH_2OH is converted to NO_2^- via both NO oxidation and the nonenzymatic reaction of NO with O_2 by a pure culture of the nitrifier *Nitrosomonas europaea* (Caranto & Lancaster, 2017). Furthermore, Maalcke et al. (2014) showed that NH_2OH is oxidized to NO and not NO_2^- by an anammox bacterium. In the AOB *N. europaea* a direct enzymatic pathway from NH_2OH to N_2O has been found (Caranto et al., 2016). In contrast, N_2O production during archaeal nitrification might result from a nonenzymatic reaction (Kozłowski et al., 2016). Only recently it was shown that N_2O can also be produced by abiotic extracellular reactions from NH_2OH , which is released from AOB, AOA, and comammox (bacterial complete ammonium oxidation) cultures (Liu et al., 2017).

So far, NH_2OH concentrations have been measured only in a few coastal sites including the Baltic Sea (Gebhardt et al., 2004; Schweiger et al., 2007), the continental shelf of Oregon (Von Breymann et al., 1982), the Yaquina River estuary, Oregon (Butler et al., 1987), and a coastal lagoon in California (Butler et al., 1988). To our knowledge the only other study that reports NH_2OH concentration measurements in the open ocean is the recently published study from Ma et al. (2018) showing three profiles from the Southwest Indian Ocean. The main objective of this study was (i) to explore the water column distribution of NH_2OH in the open ocean and (ii) to decipher its role as a potential indicator for nitrification. To this end, we present here a set of depth profiles of NH_2OH from the equatorial Atlantic Ocean and the eastern tropical South Pacific Ocean (ETSP) and compare it to N_2O , NO_3^- , and NO_2^- vertical distribution under varying O_2 conditions.

2. Materials and Methods

2.1. Study Site Description

Samples in the equatorial Atlantic Ocean were taken aboard the R/V *Maria S. Merian* cruise 18, leg 2 (MSM 18/2; Figure 1). Sampling took place in May 2011. During this period of the year, equatorial winds are

usually weak, and vertical transport is reduced (Xie & Carton, 2004). In this region, equatorial upwelling starts in June as a response to enhanced trade winds and increased vertical advection of cold, nutrient-rich waters to the surface (Philander & Pacanowski, 1986).

Samples in the ETSP off Peru were taken during two research cruises aboard the R/V *Meteor* in November (M90) and December (M91) 2012 (Figure 1). The Peruvian upwelling belongs to the four major eastern boundary upwelling systems (Chavez & Messié, 2009), and its underlying oxygen minimum zone (OMZ) is one of three major OMZs of the global ocean (Karstensen et al., 2008; Paulmier & Ruiz-Pino, 2009). The OMZ of the ETSP is a key region for marine nitrogen (N) cycling, with significant loss of fixed N by denitrification and anammox, as well as other N transformation processes like nitrification (Kavelage et al., 2013; Lam et al., 2009).

2.2. Sampling

Water samples were collected with 12 10-L Niskin bottles on a standard CTD/Rosette. The CTD system was used with double sensors for temperature, conductivity (salinity), and O₂. O₂ and nutrients (NO₃[−] and NO₂[−]) concentrations were measured on board as described in Stramma et al. (2013). The overall uncertainty for NO₃[−] and NO₂[−] measurements was ±0.1 μmol/L, and the detection limit for O₂ was 2 μmol/L.

2.3. N₂O

N₂O concentrations were already published by Arévalo-Martínez et al. (2015, 2017) and Kock et al. (2016), and further descriptions of the N₂O sampling and measurements can be found in these publications. Briefly, bubble-free samples were collected in triplicate in 20-ml brown glass vials and sealed with butyl rubber stoppers and aluminum caps to avoid any gas exchange. Ten milliliters of the sample was replaced with a synthetic air (MSM18/2) or helium (M90 and M91) headspace for each vial. To prevent microbial activity, 50 μl of a saturated aqueous mercuric chloride (HgCl₂) solution was added. After an equilibration period of at least 2 hr the samples were analyzed using a gas chromatography/electron capture detector system (Hewlett Packard 5890 Series II). Calculation of the N₂O concentrations is described in Walter et al. (2006).

2.4. NH₂OH

Dissolved NH₂OH was measured as described in Kock and Bange (2013). This improved ammonium iron (III) sulfate (FAS) conversion method is based on the conversion of NH₂OH to N₂O while NO₂[−], which results in a significant bias in the NH₂OH concentration measurements, is removed by adding sulfanilamide (SA). In detail, triplicate samples were taken from the same Niskin bottle in clear glass vials with a volume of either 56.6 ml (MSM18/2) or 60 ml (M90/91) and stored at 4 °C in the dark. Following the addition of a 10-ml headspace of synthetic air (MSM18/2) or helium (M90/91) and 400 μl of a mixture of acetic acid/SA (172-mg SA/100-ml acetic acid [glacial]) and 200-μL FAS solution (1.206-g FAS/50-ml MilliQ). Subsequently, samples were stored at room temperature for at least 24 hr before analysis of N₂O with the gas chromatography/electron capture detector system.

The NH₂OH concentration in the samples was calculated as follows:

$$[\text{NH}_2\text{OH}] = ([\text{N}_2\text{O}]_{\text{FAS}} - [\text{N}_2\text{O}]_{\text{BG}}) / \text{RC}, \quad (1)$$

$$\text{RC} = m_{\text{std}} \times 2, \quad (2)$$

where [N₂O]_{FAS} and [N₂O]_{BG} are the N₂O concentrations of samples with and without FAS conversion. m_{std} is the regression slope of the standard addition. To determine the recovery factor (RC), standard additions of NH₂OH were carried out by adding 100 μl of four stock solutions with different NH₂OH concentrations. The factor of two in the calculation of the RC results from the stoichiometry of the reaction between NH₂OH and FAS. The RC varied between 0.46 and 0.84 (M90: 0.46–0.74; M91: 0.56–0.62; MSM18/2: 0.76–0.84), which agrees well with the RC reported by Butler and Gordon (1986), 0.40–0.83; Schweiger et al. (2007), 0.44–0.64; and Ma et al. (2018), 0.68–0.80.

N₂O concentrations of the NH₂OH measurements were corrected for the change in the volume of the water phase due to the addition of the reagents, the heating of the samples from 4 °C to room temperature and due to the pressure changes from DIC release upon sample acidification. We calculated the uncertainty of the NH₂OH concentration from an error propagation based on the standard deviations of the N₂O

concentration measurements of samples with FAS ($[\text{N}_2\text{O}]_{\text{FAS}}$) and without FAS ($[\text{N}_2\text{O}]_{\text{BG}}$) addition and the determination of the RC. The uncertainties of the NH_2OH concentrations for each sample are given as error bars in Figure 2. The calculated mean uncertainty for NH_2OH was ± 2.5 nmol/L based on the error propagation. Stepwise multiple linear regressions were performed using the R statistical software package (version 3.5.0).

3. Results and Discussion

3.1. NH_2OH and N_2O Distribution

NH_2OH concentrations ranged from 2.0 to 9.5 nmol/L (MSM18/2) in the equatorial Atlantic, from 0.6 to 23.8 nmol/L (M90) in the open ocean ETSP, and from 1.5 to 20.0 nmol/L (M91) in the coastal ETSP (Figure 2). Due to the uncertainties of the NH_2OH measurements, some of the surface NH_2OH concentrations might be close to the detection limit. However, in the equatorial Atlantic and in most of the surface waters in the ETSP, NH_2OH was indeed present in low concentrations in the surface waters. The presence of NH_2OH also in surface waters is strongly indicative for active in situ production of NH_2OH . This, in turn, supports the suggestion of nitrification and potentially in situ N_2O production taking place in the upper 100 m of the water column (Dore & Karl, 1996; Zamora & Oschlies, 2014). Maximum NH_2OH concentrations of up to 23.8 nmol/L were higher compared to the only other open ocean NH_2OH study from Ma et al. (2018) in the Southwest Indian Ocean where highest measured concentrations were 6.8 nmol/L and most concentrations were below 2 nmol/L. In this study, the water column was oxic with O_2 concentrations > 50 $\mu\text{mol/L}$. However, even if we only consider NH_2OH concentrations at stations where O_2 concentrations were > 50 $\mu\text{mol/L}$, concentrations are still higher with up to 14.3 nmol/L. Butler et al. (1987) reported higher NH_2OH concentrations up to 362 nmol/L in the Yaquina River (Oregon, USA). However, in a coastal lagoon in California similar concentrations to our study ranging from 0 to 18 nmol/L NH_2OH , except two higher values of up to 175 nmol/L, were measured (Butler et al., 1988). Schweiger et al. (2007) presented measurements of NH_2OH over a whole seasonal cycle at the time series station Boknis Eck (Baltic Sea). Their NH_2OH concentrations were comparable to ours ranging from 0 to 18.5 nmol/L. Contrarily, the measurements of Gebhardt et al. (2004) in the central Baltic Sea show much higher concentrations of NH_2OH (0 to 179 nmol/L). Except of the study from Ma et al. (2018), previous NH_2OH measurements were done without the SA solution, which could have led to an overestimation of the concentrations since NO_2^- can produce significant amounts of N_2O through the decomposition of HNO_2 as a consequence of the acidification of the samples during FAS conversion (Kock & Bange, 2013). Without the addition of SA, a correlation between NO_2^- and NH_2OH could thus be an indication for NH_2OH production from the abiotic decomposition of HNO_2 . In this study, neither in the Atlantic nor the Pacific a correlation was found between NH_2OH and NO_2^- (Table 1).

Overall, NH_2OH concentrations were lower than N_2O concentrations. In the equatorial Atlantic, N_2O concentrations were comparable to former studies. Maximum N_2O values ranged from 22.3 to 24.9 nmol/L in 240 to 280 m at the equatorial stations by Walter et al. (2006), compared to 23.4 to 26.2 nmol/L in 200 m in our study and the study from Arévalo-Martínez et al. (2017). N_2O concentrations in the ETSP were higher with up to 86.1 nmol/L due to enhanced N_2O production by nitrification and/or denitrification under transient O_2 concentrations (Ji et al., 2015; Kock et al., 2016).

3.2. Equatorial Atlantic

Under oxic conditions, which we found in the equatorial Atlantic ($\text{O}_2 > 90$ $\mu\text{mol/L}$), N_2O is produced via two possible pathways, namely, nitrification and nitrifier denitrification, both of which can be carried out by nitrifying organisms (Wrage et al., 2001). Nitrifier denitrification has been suggested to play a crucial role in N_2O formation under low O_2 (Wrage et al., 2001), also by Frame et al. (2014) in the eastern South Atlantic. In the equatorial Atlantic the sampled water column was oxic and surface O_2 concentrations decreased from 200 $\mu\text{mol/L}$ to a minimum of 90 $\mu\text{mol/L}$ in 200-m depth. Under these O_2 concentrations, we can infer that nitrification is the main contributor to N_2O production. Based on N_2O distributions and $\Delta\text{N}_2\text{O}$ (N_2O anomaly) versus AOU (apparent oxygen utilization) and $\Delta\text{N}_2\text{O}$ versus NO_3^- correlations, Arévalo-Martínez et al. (2017) concluded that N_2O is mainly derived from subsurface production through nitrification in the equatorial Atlantic. In our study we used the N_2O concentrations from four out of 53

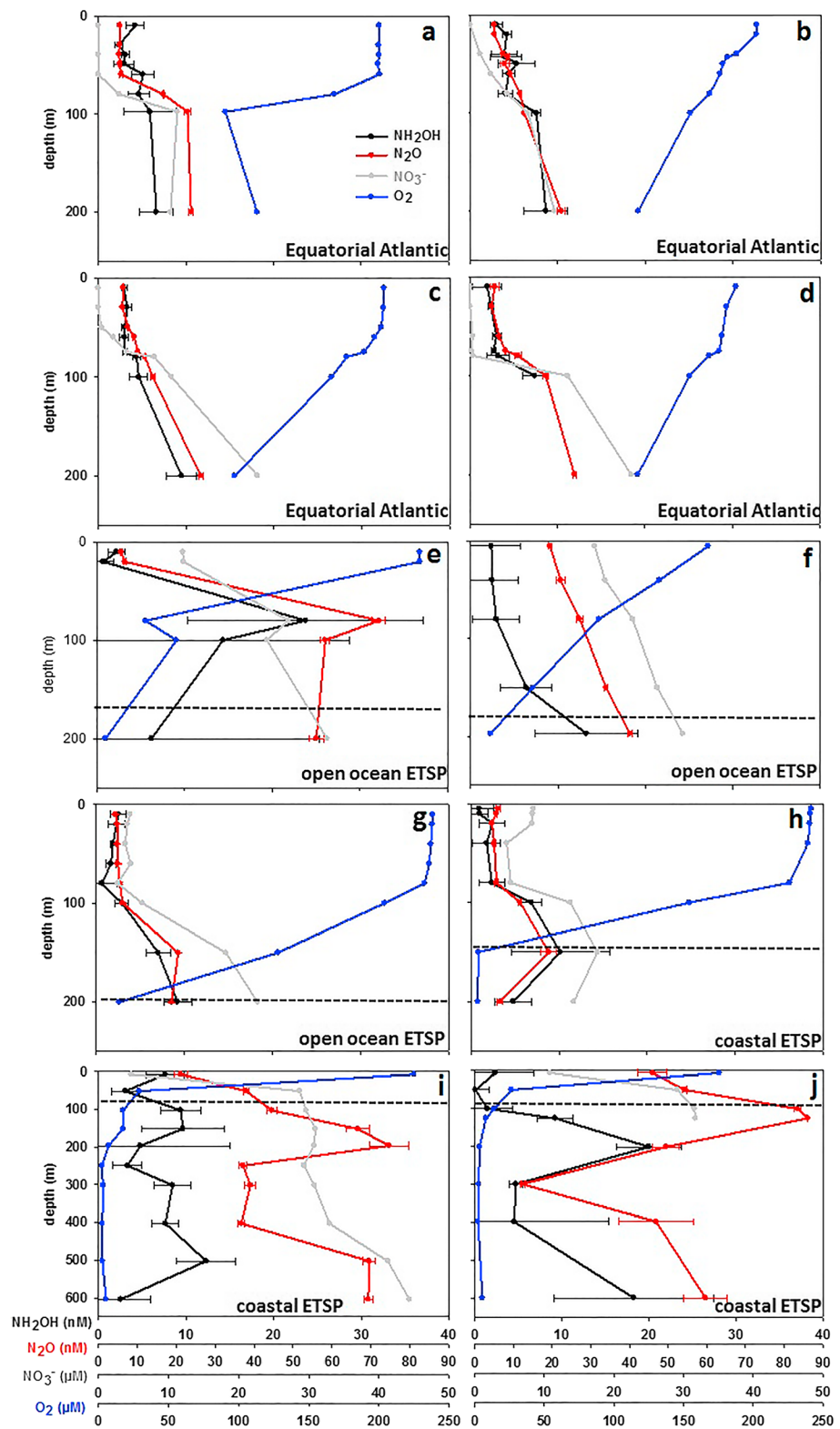


Figure 2. Vertical distribution of NH₂OH (nmol/L; black), N₂O (nmol/L; red), NO₃⁻ (μmol/L; gray), and O₂ (μmol/L; blue) at stations MSM18/2_1 (a), MSM18/2_2 (b), MSM18/2_3 (c), MSM18/2_4 (d), M90/4 (e), M90/2 (f), M90/3 (g), M90/1 (h), M91/1 (i), and M91/2 (j). The dashed line indicates the depth level of O₂ concentrations of 20 μmol/L (e.g., Paulmier & Ruiz-Pino, 2009). The error bars are shown for NH₂OH and N₂O measurements and are based on three individual sample measurements from the same Niskin bottle.

Table 1

Spearman's Rank Correlation Coefficients of NH_2OH and N_2O Concentration During the MSM18/2 (Equatorial Atlantic), M90 (Open Ocean ETSP) and M91 (Coastal ETSP) Cruises With NH_2OH , NO_3^- , NO_2^- , O_2 , and N_2O , Respectively

	NH_2OH			N_2O		
	MSM18/2	M90	M91	MSM18/2	M90	M91
NO_3^-	0.75	0.72	0.31	0.93	0.94	0.52
NO_2^-	0.01	-0.35	-0.20	0.28	-0.06	-0.02
O_2	-0.77	-0.79	-0.20	-0.83	-0.81	0.10
N_2O	0.68	0.68	0.08	—	—	—

Note. Correlation coefficients are reported at a level of confidence of $p < 0.05$.

stations that were already published in Arévalo-Martínez et al. (2017) and complemented the data set with NH_2OH concentrations at those four stations. We found a significant correlation between NH_2OH and N_2O concentrations ($p < 0.05$; Table 1), supporting the results from Arévalo-Martínez et al. (2017) that the main N_2O pathway is via nitrification. Our results furthermore suggest that active nitrification and N_2O production takes place over the full water column in the equatorial Atlantic. Additionally, parameters that are assumed to be directly connected to the production pathways of N_2O via nitrification are O_2 , AOU, and NO_3^- (Yoshida et al., 1989). NH_2OH was also correlated with AOU (Figure S1 in the supporting information). In our study N_2O was significantly correlated with O_2 and NO_3^- ($p < 0.05$; Table 1), which would be consistent with nitrification as the source of N_2O in the equatorial Atlantic.

3.2.1. NH_2OH and N_2O Discrepancy

We have to point out that the NH_2OH concentrations of 4.3 ± 1.9 nmol/L were lower than N_2O concentrations of 11.1 ± 6.1 nmol/L. This discrepancy is not necessarily contradictory to a nitrification-dominated N_2O production pathway. Unlike N_2O , NH_2OH does not accumulate in the water column due to its short half-life of only a few hours (Butler et al., 1987, 1988). Additionally, Arévalo-Martínez et al. (2017) showed, based on an inverse relationship between N_2O and sea surface temperature, that N_2O -enriched waters are transported to the surface during the upwelling season in the equatorial Atlantic. However, we cannot account how much of the N_2O is from the lateral transport of N_2O rich water and how much is produced locally. Furthermore, a significant amount of oceanic N_2O is thought to originate from archaeal rather than from bacterial nitrification (Löscher et al., 2012; Santoro et al., 2011). Although genes encoding the NH_2OH oxidoreductase complex have not been identified in AOA (Walker et al., 2010; Vajrала et al., 2013), NH_2OH is likely an intermediate in archaeal nitrification, too (Santoro et al., 2011; Vajrала et al., 2013). Still, the relative contribution of bacterial and archaeal NH_3 oxidation to nitrification and N_2O production is still not well constrained, and we cannot decipher how much of the NH_2OH is converted to N_2O during active nitrification. However, this is the first time showing that there is a significant correlation between NH_2OH and N_2O in the open ocean. In areas like the equatorial Atlantic where nitrification is the major pathway of N_2O formation (Arévalo-Martínez et al., 2017; Walter et al., 2006; Yoshida et al., 1989), NH_2OH can be, therefore, interpreted as an indicator for active nitrification.

3.3. Eastern Tropical South Pacific

The ETSP is one of the most important oceanic regions for N_2O emissions to the atmosphere (Arévalo-Martínez et al., 2015). Anoxic conditions can be found in large parts of the water column of the ETSP and NH_4^+ , NO_2^- , and NO_3^- are present in the steep upper oxycline, supporting both nitrification and denitrification taking place in close proximity. During M90 and M91, O_2 concentrations rapidly decreased to 2.5 $\mu\text{mol/L}$ (Figure 2) in the ETSP. N_2O profiles typically show a two-peak structure with pronounced maxima in the upper and lower oxycline and N_2O depletion in the OMZ core. This can be explained by enhanced N_2O production by nitrification and denitrification at the boundaries of the OMZ and by N_2O consumption through denitrification in the core of the OMZ (Bange et al., 2001; Codispoti & Christensen, 1985). Rates of N_2O production in the OMZ of the ETSP close to our study area showed that the highest N_2O production rates from both nitrification and denitrification contribute to peak N_2O concentrations in the water column with denitrification being the main N_2O production pathway (Ji et al., 2015). Especially in the coastal waters off Peru, where active upwelling leads to ventilation of the water column on the one hand and strong remineralization leads to rapid O_2 consumption on the other hand, extreme N_2O accumulation, most likely due to extraordinarily high N_2O production from denitrification, was observed (Kock et al., 2016). At coastal stations during M91, where besides nitrification, denitrification is a major N_2O production pathway (Ji et al., 2015; Kock et al., 2016), the correlation between NH_2OH and N_2O is not significant. Furthermore, stepwise multiple regressions demonstrated that N_2O , O_2 , and NO_3^- were not correlated in the coastal waters, which is in line with the results from all coastal stations sampled during this and the following campaigns (M92 and M93) to the ETSP (Arévalo-Martínez et al., 2015; Kock et al., 2016).

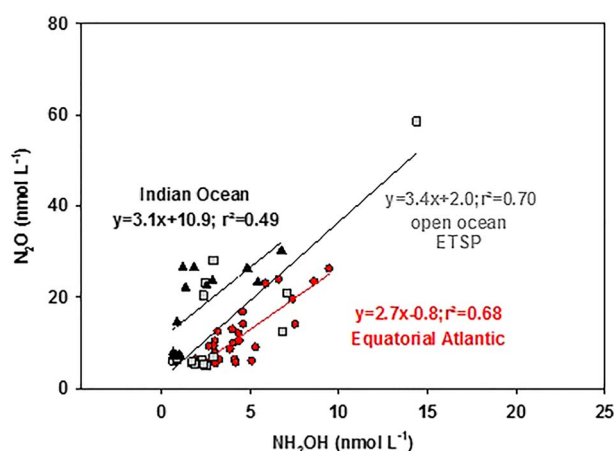


Figure 3. NH_2OH (nmol/L) versus N_2O (nmol/L) for the equatorial Atlantic (black dots, cruise MSM 18/2), the ETSP (light gray squares, cruise M90), and the Indian Ocean (dark gray triangles) for samples with $\text{O}_2 > 50 \mu\text{mol/L}$ and their regression lines. Data from the Indian Ocean are from Ma et al. (2018).

At offshore stations linear relationships for $\Delta\text{N}_2\text{O}$ and AOU have been identified in oxic waters of the ETSP (with O_2 concentrations $> 50 \mu\text{mol/L}$; Arévalo-Martínez et al., 2015; Kock et al., 2016; Ryabenko et al., 2012), which is expected when nitrification is the dominant process for N_2O production (Nevison et al., 2003). An increasing slope of the $\Delta\text{N}_2\text{O}/\text{AOU}$ relationship with increasing AOU could be an indicator for additional N_2O production from denitrification or nitrifier denitrification, however. At the stations sampled for NH_2OH during M90, we indeed observed a significant correlation between N_2O and O_2 and N_2O and NO_3^- ($p < 0.05$; Figure 2 and Table 1) in the upper oxycline. Similar to the equatorial Atlantic, a significant positive correlation was also observed between NH_2OH and N_2O at the offshore stations pointing toward active nitrification contributing to the N_2O accumulation in this area.

3.4. General NH_2OH Distribution in the Open Ocean

Comparing our results from the Equatorial Atlantic and the open ocean ETSP (M90) with the results from Ma et al. (2018) from the SW Indian Ocean, we find a similar relationship of 1:3 for NH_2OH to N_2O in all three areas for samples with O_2 concentrations $> 50 \mu\text{mol/L}$ (Figure 3). In general,

NH_2OH concentrations were $32 \pm 18\%$ of the N_2O concentrations. Since we only find a correlation between NH_2OH and N_2O in areas where nitrification is the main N_2O production pathway, we only included samples with O_2 concentrations $> 50 \mu\text{mol/L}$. This O_2 concentration was chosen, since former studies found a clear positive correlation between $\Delta\text{N}_2\text{O}$ and AOU, which is an indication for nitrification as the main N_2O production pathway, at O_2 concentrations $> 50 \mu\text{mol/L}$ (e.g., Arévalo-Martínez et al., 2015; Kock et al., 2016; Ryabenko et al., 2012; Walter et al., 2006). Due to this, samples from the coastal ETSP are not included in this comparison. Overall, this comparison indicates that there is a relative uniform global relationship between NH_2OH to N_2O in areas where nitrification is the main N_2O production pathway.

4. Conclusions

In this study, NH_2OH concentrations showed a significant correlation with N_2O concentrations in two different open ocean areas, where also positive linear $\Delta\text{N}_2\text{O}/\text{AOU}$ relationships can be found. This is consistent with the assumption that under oxic conditions, nitrification is the main N_2O production pathway and that active nitrification contributes to the local N_2O inventory. This is further supported by the fact that N_2O is positively correlated with NO_3^- , the final product of nitrification in those oxic waters (Walter et al., 2006; Yoshida et al., 1989). However, when the N_2O distribution in the water column is strongly influenced by denitrification as in the oxygen-deficient waters of the ETSP (Ji et al., 2015), no relationships can be found between NH_2OH and N_2O . Our findings indicate that besides the straightforward interpretation of the linear $\Delta\text{N}_2\text{O}/\text{AOU}$ relationship as an indicator for N_2O formation via nitrification, NH_2OH may be useful as an indicator for active nitrification and in situ N_2O production. Even though NH_2OH concentrations in the upper 100 m of the water column were low, its presence in the surface points toward nitrification in the upper 100 m, where until now no direct evidence of N_2O production was found. Overall, our results point toward a ratio of 1:3 between NH_2OH and N_2O in open ocean areas when O_2 concentrations were $> 50 \mu\text{mol/L}$. To further quantify the in situ N_2O production from NH_2OH , the molecular mechanisms and the stoichiometry of the NH_2OH conversion to N_2O by archaeal and bacterial nitrifiers need to be investigated in more detail.

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